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(54) COATED WELDING ELECTRODE CONTAINING CHROMIUM

(71) We, KOBE STEEL LTD., a Body Corporate organized under the laws of Japan, of 3—18, 1-chome, Wakinohama-cho, Fukiai-ku, Kobe City, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a consumable arc welding electrode and more particularly to a coated welding electrode containing chromium in which the content of Na_2O and K_2O in the flux coating is limited to a low level, whereby the amounts of fumes generated at the welding step, especially the amounts of toxic soluble Cr contained in such fumes, are suppressed or minimized.

Our Japanese Patent Publication No. 20477/63 discloses an attempt to generate non-toxic fumes in a welding operation which uses a low hydrogen welding electrode by reducing the content of K based on the relationship between CaF_2 and K.

U.S. Patent No. 2,983,632 discloses a coated welding electrode involving a flux which comprises titanium, limestone, iron powder and a binder. At least 1% of sodium silicate (Na_2SiO_3) based on the total flux was normally present.

A flux cored electrode (composite wire) is disclosed in our U.S. Patent No. 3,531,620 as the welding material in which the content of (Na_2O+K_2O) is lower than 1% based on the flux. In this flux cored electrode, however, since the flux is supported by a metal hoop, it is unnecessary to apply the flux around core by using a binder as in the case of a flux coated electrode.

The present invention provides a chromium-containing coated welding electrode in which the amounts of fumes generated at the welding step, especially of toxic soluble Cr contained in the fumes, are suppressed or minimized.

In accordance with the present invention there is provided a chromium-containing coated consumable arc welding electrode containing at least 0.5% of Cr based on the total weight of the welding electrode and comprising a metal core and a flux coating, wherein the flux coating contains Na_2O and/or K_2O but, to reduce the Na and K components in the flux coating the (Na_2O+K_2O) content in the flux coating is below 1% based on the total weight of the flux coating, and wherein a colloidal solution in which a disperse phase containing at least one of the oxides of Si, Al, Zr, B, P, Ti, Mg, Ca, Th and Fe constitutes from 1% to 90% by weight of the total solution is used as a binder of the flux coating.

The chromium may be in at least one of the metal core and the flux coating.

Reference is now made to the accompanying drawing which is a graph illustrating the relationship between the amount of (Na_2O+K_2O) contained in a flux and the amount of soluble Cr contained in fumes generated when welding is carried out by using a chromium-containing coated electrode.

Chromium-containing coated welding electrodes are now used for welding stainless steel materials of the Ni—Cr system and materials of the Cr—Mo system, and also as welding materials for hard facing.

Stainless steel materials are now used broadly in various industrial fields such as the petrochemical industry, the fiber industries and the atomic power industry

because stainless steels have excellent corrosion resistance, oxidation resistance and heat resistant, and have good processability and good mechanical properties, and it is expected that demands for these stainless steel materials will increase in the future. Accordingly, it is also expected that demands for welding materials for such stainless steel materials will increase.

Low alloy, heat resistant steels and heat resistant alloys are used for high-temperature, high-pressure operations conducted mainly in thermoelectric power plants and petrochemical industries. It is therefore expected that demands for materials of the Cr—Mo system will increase in the future. Accordingly, it is also expected that welding materials for such materials of the Cr—Mo system will increase.

Further, welding materials for hard facing are now used in various fields for construction work, mining and agriculture, and it is expected that their range of applications will be expanded henceforth.

Chromium-containing welding materials are thus used in various industrial fields and their excellent properties are fully utilized. Fumes are inevitably generated from welding materials at the welding step, and, as a result of analytical experiments made by us, we have found that so-called soluble Cr which is soluble in water and is now regarded as being toxic is contained at a concentration of several percent in fumes generated from chromium-containing welding materials. Various contrivances for removing fumes are now made at welding spots so as to improve the working environment, and although the working environment has been significantly improved by these means for removing fumes from welding spots, it is preferred to prevent beforehand the generation of toxic substances such as soluble Cr.

Therefore, we have sought to clarify why and how soluble Cr is contained in fumes from chromium-containing welding materials, and, as a result of the X-ray diffraction analysis of such fumes, we have confirmed that compounds of Cr with Na and K are contained in these fumes. Thus, we have found that, when Na or K is co-present with Cr in a welding material, soluble Cr is generated in the fumes. For confirmation, the content of soluble Cr in fumes generated when welding was carried out using a bare core containing 20% of Cr was analytically compared with the content of soluble Cr contained in fumes generated when welding was carried out by using an electrode formed by coating the above core with a coating including water glass [(Na_2O+K_2O) content=13%, SiO_2 content being 13%. It was found that the soluble Cr content was below 0.01% in the former case while the soluble Cr content was as high as 2.75% in the latter case.

Based on these findings, we have succeeded in reducing the soluble Cr content in the fumes to a minimum level by reducing the contents of Na and K as much as possible in the flux of a flux-coated, chromium-containing welding electrode.

Water glass containing at least one of Na_2O and K_2O is ordinarily used as a binder for a coating flux of a coated welding electrode, and slag-forming agents containing Na_2O and K_2O such as feldspar and mica are often used and also carbonates of Na and K are used.

As pointed out hereinbefore, the presence of Na and K components in the flux is a cause of the generation of soluble Cr. However, since the Na or K component is effective as an arc stabilizer or as one component of a binder, it is preferred that Na and K components should be present in small amounts. Therefore, it is necessary to clarify the relation between the content of Na and K components and the amount of soluble Cr generated. Accordingly, we have made the following experiments.

Experiment 1

Various chromium-containing cores having a diameter of 5.0 mm and a length of 400 mm were coated with a flux comprising limestone, rutile, fluorite, metallic Cr and feldspar by using a binder (SiO_2 content=20%, Na_2O content ≦0.35%) so that the diameter of the resulting coated electrode was 7.5 mm. Chromium-containing test electrodes were prepared. The Cr contents in the core and flux of each electrode and the Na_2O and K_2O contents in the flux (inclusive of the binder) were as shown in Table 1 below. By using each welding electrode, welding was carried out under the conditions indicated below, and fumes were collected and analysed according to the methods described below.

(1) Welding conditions:
170 A, 22—27 V, AC.

(2) Base metal:

19 mm (thickness)×75 mm (width)×400 mm (length) (mild steel buttered with the test electrode).

(3) Method of collecting fumes:

Welding was carried out in an iron box open in its lower portion and having a high volume air sampler in the upper portion, and generated fumes were sucked in by the high volume air sampler and collected on a filter paper. After completion of the welding, the filter paper was taken out and fumes were gathered and analysed. The filter paper used was as follows:

Material: glass fiber
Shape: 8 inches×12 inches
Weight: about 4000 mg

(4) Analysis method:

Soluble Cr in fumes: atomic absorption method Na_2O and K_2O in the flux: atomic absorption method.

(5) Results:

The results obtained were as shown in Table 1 and the accompanying drawing.

TABLE 1

System	Sample No.	Cr Content (wt.%) in Core	Cr Content (wt.%) in coated Electrode	(Na_2O+K_2O) Content (wt.%) in Flux	Soluble Cr Content (wt.%) in Fumes
5-Cr	1	5.5	5	0.29	0.07
5-Cr	2	5.5	5	0.55	1.11
5-Cr	3	5.5	5	1.13	1.39
5-Cr	4	5.5	5	1.81	1.40
5-Cr	5	5.5	5	4.84	1.60
15-Cr	1	19.0	15	0.31	0.25
15-Cr	2	19.0	15	0.63	2.74
15-Cr	3	19.0	15	1.16	2.97
15-Cr	4	19.0	15	2.33	3.41
15-Cr	5	19.0	15	4.73	3.55
25-Cr	1	26.5	25	0.22	0.99
25-Cr	2	26.5	25	0.50	4.08
25-Cr	3	26.5	25	0.86	4.43
25-Cr	4	26.5	25	1.20	4.49
25-Cr	5	26.5	25	4.75	5.25
40-Cr	1	26.5	40	0.21	1.20
40-Cr	2	26.5	40	0.58	5.10
40-Cr	3	26.5	40	0.89	5.48
40-Cr	4	26.5	40	1.73	5.75
40-Cr	5	26.5	40	3.10	6.74

In Table 1, each value of the (Na_2O+K_2O) content is a value of the total content of (Na_2O+K_2O) in the coating flux inclusive of the binder. This content was adjusted by controlling the amount of feldspar added.

Experiment 2

Cores having a diameter of 4.0 mm and a length of 350 mm were coated with a flux as indicated in Table 2 below by using a binder (SiO_2 content=20%, Na_2O content ≦0.35%) to prepare coated electrodes for stainless steel D308 according to JIS Z-3221. The welding test was carried out as described below.

(1) Welding conditions:

140 A, 20—25 V, AC.

(2) Base metal:

19 mm (thickness)×75 mm (width)×400 mm (length) (formed by buttering mild steel with D308).

(3) Methods of collecting and analysing fumes:
As described in Experiment 1.

(4) Results:
The results obtained were as shown in Table 3 and in the drawing.

TABLE 2

Sample No.	Flux Composition (parts by weight) limestone	fluorite	rutile	metallic Cr	electrolytic Mn	mica	Binder (cc per 100 g of solvent)
1	20	5	48	7.5	5	—	15.5
2	20	5	48	7.7	5	3	16.0
3	20	5	48	8.2	5	10	18.3
4	20	5	48	9	5	20	18.4
5	20	5	48	10.5	5	35	17.0

TABLE 3

Sample No.	Cr Content (wt.%) in Entire Welding Electrode	(Na_2O+K_2O) Content (wt.%) in Flux	Soluble Cr Content (wt.%) in Fumes
1	16	0.28	0.07
2	16	0.58	2.22
3	16	1.18	3.00
4	16	2.00	3.75
5	16	3.08	3.91

As will be particularly apparent from the accompanying drawing, when the content of (Na_2O+K_2O) in the flux is below 1%, the amount of soluble Cr in the fumes decreases fairly sharply. When the content of (Na_2O+K_2O) is above 1%, there is observed a tendency that the amount of soluble Cr decreases with a decrease in the content of (Na_2O+K_2O), but this decrease is not conspicuous. This soluble Cr-reducing effect is more conspicuous in a lower Cr system, but is commonly attained in all the systems ranging from the 5-Cr system to the 40-Cr system. Such systems being exemplified hereinbefore. Accordingly, it will readily be understood that, if the content of (Na_2O+K_2O) is reduced below 1%, the soluble Cr content in the fumes can be remarkably reduced. Further, it will be apparent that, even if the content of (Na_2O+K_2O) is below 1%, the gradient of each curve changes sharply at a point corresponding to an (Na_2O+K_2O) value of 0.75%. Accordingly, we prefer that the content of (Na_2O+K_2O) should be reduced below 0.75%.

Moreover, in the region where the content of (Na_2O+K_2O) is below 0.5%, each curve is substantially vertically linear. Thus, it is seen that, if the content of (Na_2O+K_2O) is reduced below 0.5%, the amount of soluble Cr in the fumes can be drastically reduced. It is most preferred that the content of (Na_2O+K_2O) should be reduced to values approaching zero. Thus, water glass having a much reduced (Na_2O+K_2O) content may be used as the binder, and feldspar or the like containing Na_2O and K_2O is not added but silica sand is used as the SiO_2 source.

As stated previously, the binder for the coated welding electrode is a colloidal solution comprising a disperse phase containing at least one of the oxides of Si, Al, Zr, B, P, Ti, Mg, Ca, Th or Fe. A dispersion medium may be water or an organic solvent, and a stabilizer may be an alkali metal compound, an ammonium compound, an amine, organic acid or inorganic acid. Specifically, the colloidal solution may contain lithium silicate, amine silicate, colloidal silica or alumina sol. The above mentioned metal oxide containing disperse phase may be used alone or in the form of a mixture of two or more of them. If the amount of the disperse phase is below 1% based on the total weight of the binder, the binding effect is insufficient. On the other hand, if the amount of the disperse phase is above 90% of the total weight of the binder, the fluidity or stability of the binder is degraded, gelation readily takes place and the coating property of the binder is reduced. Moreover, strain is readily caused in the coating at the drying step. The kind of dispersion medium that can be used for the formation of the above colloidal solution in the present invention is not particularly critical, but water or an organic solvent is optionally chosen and used.

In welding electrodes used for the above-mentioned experiments, since compounds having an arc-stabilizing activity, such as carbonates, fluorides and titanium oxide were included, even if the amounts of Na_2O and K_2O were very small, the arc did not become unstable. In view of the foregoing, it is seen that, even in the case where Na_2O and K_2O have to be incorporated as arc stabilizers in the Cr-containing welding electrode of the present invention, their content must be reduced below 1% and that, in the case where other arc-stabilizing substances can be used, the content of Na_2O and K_2O in the flux coating is reduced to below 1%, preferably below 0.5%, and more preferably to values approaching zero.

As will be apparent from the foregoing illustration, according to the present invention, by controlling the co-presence of Cr and Na and K components under certain conditions, the amount of soluble Cr generated in fumes can be drastically reduced. Therefore, even at a welding spot where the provision of a fume sucking treatment apparatus is not feasible or allowed, the problem of operational safety can be solved. It is to be noted that, when such fume sucking apparatus is used, the disposal of the collected fumes normally causes difficulties. Therefore, the present invention makes a significant contribution to the improvement of the working environment.

WHAT WE CLAIM IS:—

1. A chromium-containing coated consumable arc welding electrode containing at least 0.5% of Cr based on the total weight of the welding electrode and comprising a metal core and a flux coating, wherein the flux coating contains Na_2O and/or K_2O but to reduce the content of Na and K components in the flux coating the (Na_2O+K_2O) content in the flux coating is below 1% based on the total weight of the flux coating, and wherein a colloidal solution in which a disperse phase containing at least one of the oxides of Si, Al, Zr, B, P, Ti, Mg, Ca, Th and Fe constitutes from 1% to 90% by weight of the total solution is used as a binder of the flux coating.

2. A chromium-containing coated welding electrode as set forth in Claim 1, wherein the (Na_2O+K_2O) content in the flux coating is below 0.75% based on the total weight of the flux coating.

3. A chromium-containing coated welding electrode as set forth in Claim 2, wherein the (Na_2O+K_2O) content in the flux coating is below 0.5% based on the total weight of the flux coating.

4. A chromium-containing coated welding electrode as claimed in Claim 1 and substantially as herein described with reference to the accompanying drawing and/or either of the specific examples.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*